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HYDROTREATING OF OIL FROM EASTERN OIL SHALE

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INTRODUCTION

Oil shale provides one of the major fossil energy reserves for the United States. The quantity of reserves in oil shale is less than the quantity in coal, but is much greater (by at least an order of magnitude) than the quantity of crude oil reserves. With so much oil potentially available from oil shale, efforts have been made to develop techniques for its utilization. In these efforts, hydrotreating has proved to be an acceptable technique for upgrading raw shale oil to make usable products (1). The present work demonstrated the use of the hydrotreating technique for upgrading an oil from Eastern oil shale.

DESCRIPTION OF TESTS

The pilot plant, which had a capacity of slightly over one gallon per day, approached isothermal operation using conventional fixed-bed, trickle-flow hydrotreating. Hydrogen was recycled and the pilot plant had necessary provisions to avoid plugging by ammonium sulfides.

Tests were made using a commercial catalyst at 2300 psig and 0.4 LHSV (i.e., volumes of hydrocarbon feed/volume of catalyst/hour) with a hydrogen flow rate of 6000 SCF/B. The temperature was varied between 720 and 800°F.

The feed for these tests was an oil recovered from Indiana New Albany shale using the Hytort Process. (Details of retorting are outside the scope of this paper.) Although this oil is probably different from that which would be obtained in an optimized process, its key properties are representative of those one would expect to obtain. These properties are given in Table I. In addition, properties of a Western shale oil, obtained by Phillips, are shown for comparison. Many of the properties of the Eastern oil are similar to the properties of the Western oil, but differences are present. The most significant differences are that the Eastern oil has lower viscosity, lower pour point, lower elemental hydrogen content, lower arsenic content, lower portion boiling above 1000°F and higher portion boiling below 400°F than does the Western oil.

DISCUSSION OF RESULTS

Excellent removal of nitrogen was obtained in single-stage hydrotreating without feed pre-processing. As shown by the data in Figure 1, the total nitrogen content of the product decreased from 800 to 70 wppm (96 to 99.6% removal) as the temperature was increased from 720 to 800°F. A temperature of 783°F was needed to reduce the nitrogen content of the shale oil from the 1.89 wt % in the feed to 0.01 wt % in the product. In other Phillips tests with oil from Western shale, the nitrogen content was reduced to 0.01 wt % at slightly milder operating conditions.

The basic nitrogen content of the product was approximately half the total nitrogen content. Since the basic nitrogen content of the feed was 47% of the total nitrogen content, reductions in basic and total nitrogen were comparable in these tests. Removals might not be comparable, however, at a significantly different operating pressure.

A correlation between temperature and hydrogen consumption is shown in Figure 2. As the temperature was increased from 720 to 800°F, chemical hydrogen consumption increased from 1950 to 2300 SCF/B. To produce product with a nitrogen content of 100 wppm, chemical hydrogen consumptions are lower than these obtained with the Eastern oil. However, the Eastern oil has a lower boiling range; thus, it may be a more valuable synthetic crude.

Data on yields are shown in Figure 2. On a weight basis, the yield of liquid product decreased as the temperature was increased (from 97 to 94 wt % of feed as temperature increased from 720 to 800°F). On a volume basis, the maximum yield of liquid product (almost 107 vol % of feed) was obtained at about 740°F, with only slightly lower yields at higher or lower temperatures. As temperature was increased (thereby giving more severe operating conditions), smaller

percentages of the liquid product were in the higher boiling ranges. The amount of material boiling above 650°F decreased by about 18 wt % of feed to the hydrotreater when operating at 720°F and by about 30 wt % of feed when operating at 800°F. The material cracked into all lower boiling ranges. At a temperature of 720°F, the amount boiling in the C₅-400°F boiling range increased by 12 wt % of the feed and at 800°F it increased by 19 wt % of the feed. At 720°F about 1.5 wt % of feed was cracked to C₁ through C₄ hydrocarbons. This amount increased to about 4.7 wt % when temperature increased to 800°F.⁴ The amount in the 400 through 650°F boiling range appeared to increase by 3 or 4 wt % of the feed. Data scatter obscured any possible correlation between variation in amount of increase in 400-650°F fraction and severity of hydrotreating.

TABLE I
PROPERTIES OF SHALE OILS

	From Eastern Oil Shale	From Western Oil Shale
API gravity at 60/60°F ^a	17.0	19.1
Ramsbottom carbon residue, wt %	1.45	2.77
Viscosity, cSt at 40°C	7.65	45.57
Bromine no.	68	56
Pour point, °F	-9	80
Total nitrogen content, wt %	1.89	2.12
Basic nitrogen, content, wt %	0.88	1.10
Sulfur content, wt %	0.99	0.85
Oxygen content, wt %	1.25	1.39
Water content, wt %	0.39	0.59
Elemental carbon content, wt %	85.08	83.83
Elemental hydrogen content, wt %	10.05	11.23
Nickel content, wppm	2.3	6.7
Vanadium content, wppm	0.3	1.4
Arsenic content, wppm	10.3	34.5
Portion boiling below 400°F, wt %	19.5	3.2
Portion boiling between 400 and 650°F, wt %	36.4	25.9
Portion boiling between 650 and 1000°F, wt %	41.6	48.4
Portion boiling above 1000°F, wt %	2.5	22.5

- a. Corrected to 60/60°F from the measurement temperature of 33.5°C using API Measurement Tables for petroleum.

The data point at 800°F was largely ignored in drawing some of the curves (i.e., yield of C₁ to C₄ hydrocarbons, yield of C₅ and heavier and increase in amount of C₅ to 400°F material) in Figure 2 because the data are believed to be incorrect. An operating problem caused the light hydrocarbon stream to be caught in a non-cooled container, from which some of the light hydrocarbons weathered and were lost.

The cracking and removal of heteroatoms caused a significant increase in the API Gravity. As shown in Figure 2, the API Gravity of the liquid product varied between 31.5 and 36.7 as the temperature varied between 720 and 800°F.

CONCLUSIONS

1. An excellent synthetic crude can be produced by single-stage hydrotreating of oil from Eastern shale.
2. Operation to produce a product containing 100 ppm nitrogen (a) requires a temperature of about 783°F with new catalyst at 2300 psig, 0.4 LHSV and 6000 SCF/B flow of hydrogen; (b) chemically consumes 2250 SCF/B of hydrogen; (c) cracks about 4 wt % of feed into C₁ through C₄ hydrocarbons; and (d) reduces amount boiling above 650°F by about 27 wt % of feed.
3. In comparison with other Phillips tests using Western shale oil, the Eastern shale oil requires more severe hydrotreating conditions to lower the nitrogen content to 0.01 wt % than does the Western oil and chemical hydrogen consumption is higher when hydrotreating the Eastern oil to an equivalent nitrogen content.

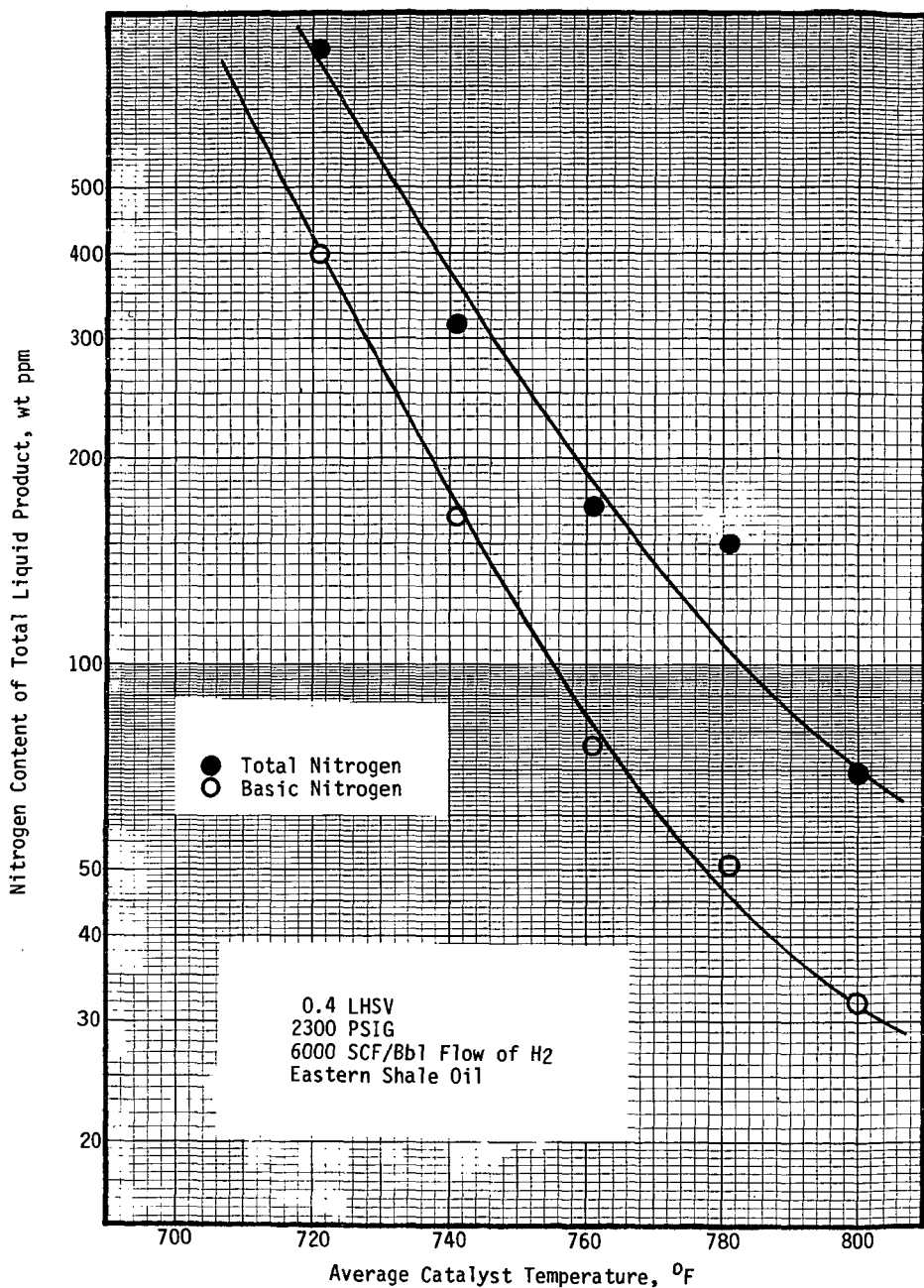


Figure 1
CORRELATION BETWEEN CATALYST TEMPERATURE AND NITROGEN CONTENT OF LIQUID PRODUCT

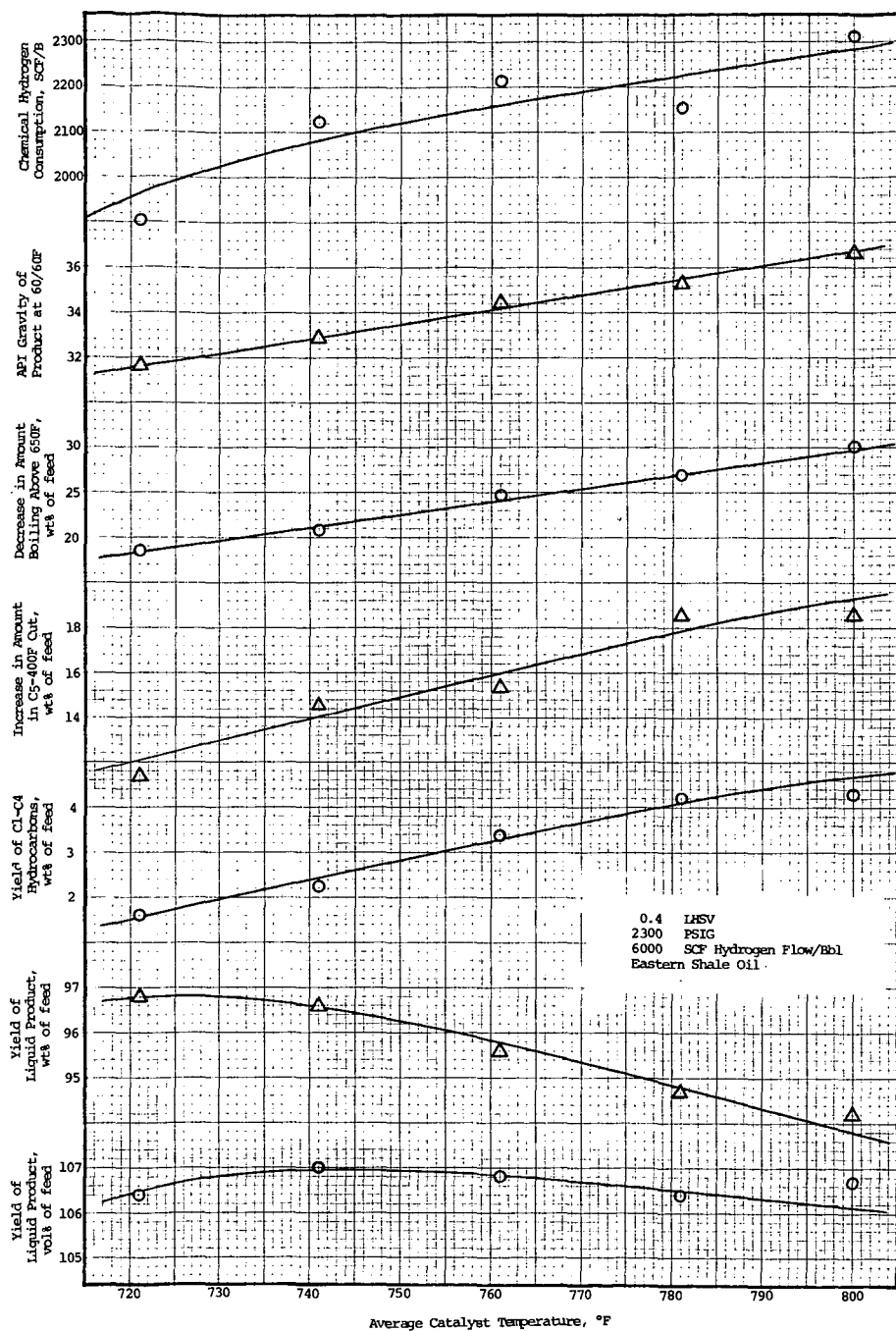


Figure 2

CORRELATION BETWEEN CATALYST TEMPERATURE AND SELECTED OTHER ITEMS

LITERATURE CITED

- (1) Sullivan, R. F. , Stangeland, B. E. , Rudy, C. E. , Green, D. C. and Frumkin, H. A. ,
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